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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Production of thioether alcohols or thioether carboxylic acids

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

We have found that thioether alcohols or thioether carboxylic acids are obtained advantageously by reacting an olefinic hydrocarbon in the presence of oxygen with a saturated mercaptoalcohol or mercaptocarboxylic acid in the presence of the thioether alcohol or thioether carboxylic acid which is the expected reaction product.

Olefines having one or more double bonds in terminal position and also olefines having one or more double bonds between two carbon atoms not occupying terminal positions may be used for the new process. They may be linear or branched aliphatic, cycloaliphatic or araliphatic hydrocarbon radicals. Mixtures of these olefinic hydrocarbons in any proportions may also be used. Preferred olefines contain one or two double bonds. Specific examples are: n-butene-(1), n-butene-(2), isobutene, butadiene, hexene, heptene, diisobutene, decene, dodecane, tridecene, tetradecene and hexadecene.

The preferred mercaptoalcohols or mercaptocarboxylic acids for the new process contain the carbon atoms in a linear saturated chain or, when the number of carbon atoms is more than three, in a branched saturated chain or linked together to form a saturated ring; moreover, they may contain in any position at least one hydroxyl group and/or carboxyl group and at least one thiol (mercapto) group. The mercapto compounds may also contain additional groups or atoms, such as oxygen atoms or sulphur atoms, which are inert under the reaction conditions.

Under the reaction conditions, the mercapto compounds add on smoothly to the olefinic hydrocarbons adding one mole of mercapto compound to one double bond. The two reactants may in fact be used in molar proportions which vary within wide limits, but the optimum molar ratios are those about 1:1.

The new process is carried out in the presence of oxygen and in liquid phase. It is simplest to pass oxygen or a gas containing molecular oxygen and other gas which is inert through the reaction mixture. Air is an example of a suitable gas. The oxygen is advantageously used in an amount of from 0.01 to 10 litres per kilogram of reacted olefine. A particularly rapid reaction is achieved when the reactants are kept simultaneously in movement, which promotes mixing, for example in a stirred vessel, particularly when the reactants have little or no miscibility with each other.

The decisive advance of the new process lies in the use of the expected reaction product, i.e. the thioether alcohol or thiocarboxylic acid formed. This reaction product may serve as a solvent. Further inert solvents are not generally used, although a certain amount thereof, for example up to 90% or more by weight of the weight of reaction product, has no appreciable disadvantageous effect on the course of the reaction. It is important that the olefine and the mercapto compound should react with each other in a medium which contains from the start the expected reaction product. The reaction is thus quickly initiated and proceeds smoothly and with good yields. When the end product is not present, however, a varying incubation period is observed, often lasting days, before the reaction suddenly

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starts and proceeds violently. The reaction medium may contain very small amounts of the end product, for example only 0.1% by weight of the weight of the entire reaction mixture. Contents of more than 1% by weight, and indeed up to 50%, particularly up to 30%, by weight are generally used when a batch method is adopted and up to 99%, particularly up to 50%, when the process is carried out continuously. Continuous operation is preferred, for example in a loop to which feedstock is continuously supplied and from which reaction mixture is continuously withdrawn.

It is advantageous to use temperatures of from −50°C to +100°C, particularly from 0° to 50°C, and pressures of from 0.5 to 10 atmospheres. Good cooling is advisable in most cases in order to remove heat of reaction which is often considerable.

High reaction speeds are achieved with the new process and in particular a very smooth and uniform course of reaction. Ten minutes to two hours is usually sufficient for completion of the reaction, the course of which may be followed by determining the iodine number and/or the hydroxyl number of the reaction mixture. The thioether alcohols and thioether carboxylic acids are generally obtained very pure and in many cases may be used for further reactions without special purification.

The compounds obtainable according to the new process have a variety of applications as intermediates for the production of biocides, particularly insectisides and herbicides, and also for the production of corrosion inhibitors and anion-active, cation-active and nonionic surfactants, such as detergents, textile assistants, emulsifiers, solubilisers and the like.

The invention is illustrated by the following Examples in which the parts specified are by weight, unless otherwise stated. Parts by volume bear the same relation to parts by weight as the litre to the gram.

Example 1

168 parts of hexadecene, 58.5 parts of β-mercaptoethanol and 50 parts of n-hexadecyl-β-hydroxyethyl sulphide are vigorously mixed in a stirred vessel at 50°C while passing a current of air through at the rate of 1 part by volume per hour. After about one and a half hours, the reaction mixture has become homogeneous, and the temperature, with intense cooling, rises to about 60° to 70°C. About three hours later the reaction has been completed and this may be detected by titrating a sample with iodine solution

(consumption 0.1 ml of $\frac{N}{10}$ iodine solution per gram of reaction product) or by determining the hydroxyl number (183). The values show that the reaction product is very pure (degree of purity 98 to 99%).

Example 2

168 parts of an octadecene having a mid-position double bond, 52 parts of β-mercaptoethanol and 60 parts of iso-octadecyl-β-hydroxyethyl sulphide are vigorously mixed as described in Example 1 at 30°C while passing through a current of air at 30 parts by volume per hour. The temperature of the reaction mixture soon rises to about 60° to 70°C in spite of intense cooling with cold water; after about thirty minutes the reaction mixture has become homogeneous and after another fifteen minutes about half of the mercaptoethanol present has already been converted. The reaction product consumes

0.15 ml of $\frac{N}{10}$ iodine solution per gram and the hydroxyl number is 165.

WHAT WE CLAIM IS:—

1. A process for the production of thioether alcohols or thioether carboxylic acids wherein an olefinic hydrocarbon is reacted in the presence of oxygen with a saturated mercaptoalcohol or mercaptocarboxylic acid in the presence of the thioether alcohol or thioether carboxylic acid which is the expected reaction product.

2. A process as claimed in claim 1 wherein the olefinic hydrocarbon used is n-butene-(1), n-butene-(2), isobutene, butadiene, hexene, heptene, diisobutene, decene, dodecene, tridecene, tetradecene or hexadecene.

3. A process as claimed in claim 1 or 2 wherein the mercapto compound and the olefinic compound are used in approximately equimolar amounts.

4. A process as claimed in any of claims 1 to 3 wherein oxygen or a gas containing molecular oxygen is passed through the reaction mixture.

5. A process as claimed in claim 4 wherein the amount of oxygen used is from 0.01 litre to 10 litres per kilogram of olefine reacted.

6. A process as claimed in any of claims 1 to 5 carried out substantially as described in either of the foregoing Examples.

7. Thioether alcohols or thioether carboxylic acids when obtained by the process claimed in any of claims 1 to 6.

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